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1. Title of the Invention
     Method for Manufacturing a Zn-Ni alloy plated steel plate

2. Claims
10   1. A method for manufacturing a Zn-Ni alloy plated steel
plate by using a sulfate bath as a plating electrolyte, wherein
1 to 100 mg/l of Bi^{+3} ions is added to the sulfate bath.

     2. The method for manufacturing a Zn-Ni alloy plated steel
15 plate according to claim 1, wherein each of a Ni^{2+} ion concentration
and a Zn^{2+} ion concentration in the plating electrolyte is 25 g/l
or more, a molar concentration ratio represented by $Ni^{2+}/(Ni^{2+}+Zn^{2+})$
is 0.4 or more and less than 0.6, a current density is 100 A/dm^2
or less, and a relative flow rate of a plating solution to a steel
20 plate to be plated is 1.5 m/sec or less.

3. Detailed Description of the Invention
     (Field of the Invention)
     The invention relates to a method for manufacturing a Zn-Ni
25 alloy plated steel plate. More particularly, the invention
relates to a method capable of economically manufacturing a Zn-Ni
alloy plated steel plate at a lower Ni concentration than that
used in a conventional, commonly used method. The method of the
invention is widely used in the field of manufacturing a
30 surface-treated steel plate that is used in automobile bodies and
the like.
     (Prior art)
     Recently, surface-treated steel plates have been used to
prevent corrosion of automobile bodies and the like.   The
35 surface-treated steel plates used for this purpose are required

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to have not only corrosion resistance but good shaping capability and spot weldability. A Zn-Ni alloy plated steel plate has attracted attention as one of the surface-treated steel plates that meet these requirements.

5   Zn-Ni alloy plated steel plates are usually produced by using a sulfate bath as a plating electrolyte (hereinafter, referred to as a plating solution). However, Zn-Ni alloy plating using a sulfate bath is called abnormal deposition type plating. In this Zn-Ni alloy plating, a plating layer having a target Ni

10 content cannot be obtained unless a concentration of Ni^{2+} ions that are supposed to be easily deposited in terms of a potential is significantly higher than that of Zn^{2+} ions. For example, in Japanese Patent Publication No. 62-15635, a molar concentration ratio of Ni^{2+}/Zn^{2+} is 1.5 to 4.0, and a Ni molar concentration ratio,

15 $Ni^{2+}/(Zn^{2+}+Ni^{2+})$, is as high as 0.6 to 0.8. In this case, a lot of expensive Ni^{2+} ions are required, and loss from drag-out is large, which is economically a big problem.

     In the technology disclosed in Japanese Patent Laid-Open Publication No. 62-136590, a solution need to flow between

20 electrodes in the opposite direction to the moving direction of a steel plate at a Ni molar concentration ratio of 0.4 or more, a current density of 100 A/dm^2 or more, and a solution flow rate of 1.5 m/sec or more. Moreover, when respective capacities of a current-carrying rectifier and a liquid flow pump are

25 insufficient, a plating layer having a target Ni content cannot be obtained with a low Ni molar concentration bath. Moreover, a lot of facility investment is required in order to increase the capacities of these devices. As described above, conventional methods for manufacturing a Zn-Ni alloy plated steel plate have

30 many outstanding problems.

     (Problems to be Solved by the Invention)

     It is an object of the invention to provide an effective method which solves the problems of the conventional methods for manufacturing a Zn-Ni alloy plated steel plate, especially, the

35 following two problems (i) and (ii), and which is capable of

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manufacturing a γ single-phase Zn-Ni alloy plated steel plate having a Ni content of 9 to 18 wt% even when plating is conducted using a low Ni molar concentration ratio bath at a current density of less than 100 A/dm^2 and a plating solution flow rate of less than 1.5 m/sec:

   (i) A Ni molar concentration ratio is as high as 0.6 to 0.8; and

   (ii) When a Ni molar concentration ratio is less than 0.6, a plating solution flow rate is as high as 1.5 m/sec or more, and a current density is as high as 100 A/dm^2 or more.

   (Means for Solving the Problems and Functions)

   According to the invention, a method for manufacturing a Zn-Ni alloy plated steel plate by using a sulfate bath as a plating electrolyte is characterized in that 1 to 100 mg/l of Bi^{+3} ions is added to the sulfate bath.

   As described above, Zn-Ni alloy plating using a sulfate bath is called abnormal deposition type plating. In this Zn-Ni alloy plating, a plating layer having a target Ni content such as 9 to 18 wt% cannot be obtained unless a Ni^{2+} ion concentration is significantly higher than a Zn^{2+} ion concentration. In order to solve the problems of the conventional technology, the inventors conducted various experiments and studies about a method capable of forming a plating layer having a target Ni content even when a plating bath has a low Ni^{2+} ion concentration. As a result, the inventors found that such a plating layer could be formed by adding 1 to 100 mg/l of Bi^{3+} ions to a plating bath, and thus completed the invention.

   The results of the experiments conducted by the inventors will now be described.

Plating conditions:

Plating bath:

   Zinc sulfate + nickel sulfate   380 g/l
   Sodium sulfate   40 g/l;

Current density: 50 A/dm^2;

Plating solution flow rate: 1.0 m/sec;

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Ni^{2+} molar concentration ratio, $Ni^{2+}/(Zn^{2+}+Ni^{2+})$: 0.35, 0.40, 0.50, 0.60, and 0.67; and

Plating deposition amount: 30 g/m^2

Zn-Ni plating was conducted by adding $Bi_2(SO_4)_3$ to the above basic sulfate bath so that the amount of Bi^{3+} ions in the sulfate bath varied in the range of 0 to 140 mg/l. For each sample, a Ni content of the resultant plating layer was obtained.

It should be noted that, as the applicant disclosed in Japanese Patent Laid-Open Publication No. 62-136590, both a Ni^{2+} ion concentration and a Zn^{2+} ion concentration need to be 25 g/l or more in this invention, too. This is because using the ion concentrations of less than 25 g/l will not only produce defective appearance but reduces current efficiency in high current density plating of around 100 A/dm^2, which is not practical.

The test results are shown in Table 1. The following facts can be found from the test results of Table 1:

(i) When a Ni molar concentration ratio is less than 0.4, e.g., 0.35, the amount of Ni^{2+} ions is insufficient, and it is difficult to obtain a Zn-Ni plating layer having 9 wt% or more of Ni even when Bi^{3+} ions are added;

(ii) When a Ni molar concentration ratio is 0.6 or more, a Zn-Ni plating layer having 9 wt% or more of Ni can be obtained without adding Bi^{3+} ions;

(iii) When less than 1 mg/l of Bi^{3+} ions is added, the effect of increasing a Ni content of a plating layer is not sufficient. However, when 1 mg/l or more of Bi^{3+} ions is added, the effect of increasing a Ni content of a plating layer increases as the amount of Bi^{3+} ions increases. Especially, the effect further increases as a Ni molar concentration ratio increases. However, it was found that corrosion resistance of a Zn-Ni alloy plated steel plate decreases when more than 100 mg/l of Bi^{3+} ions is added. Therefore, in the invention, addition of Bi^{3+} ions should be limited to the range of 1 to 100 mg/l; and

(iv) When 1 to 100 mg/l of Bi^{3+} ions is added to a Zn-Ni plating bath, a Zn-Ni plated steel plate having a Ni content of 9 to 18

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wt% can be obtained even at a low Ni molar concentration ratio of 0.4 or more and less than 0.6, a current density of less than 100 A/dm^2, and a solution flow rate of less than 1.5 m/sec.

Functions of adding Bi^{3+} ions in Zn-Ni alloy plating using the above sulfate bath according to the invention have not been clarified in detail yet, but can be considered as follows: by adding Bi^{3+} ions, a barrier layer of zinc hydroxide that is formed on the interface of a metal strip becomes porous, whereby normal deposition is facilitated. As a result, a γ single-phase Zn-Ni plating layer having a Ni content of 9 to 18 wt% can be obtained even when a Ni molar concentration ratio is as low as 0.4 to less than 0.6.

(Examples)

Zn-Ni alloy plating of a cold-rolled steel strip was conducted under the following conditions:

(i) Plating bath:

$NiSO_4 \cdot 6H_2O$

$ZnSO_4 \cdot 7H_2O$

Ni molar concentration ratio: 0.35 to 0.67

Na_2SO_4: 40g/l

$Bi_2(SO_4)_3$: 0 to 112 mg/l of Bi^{3+} ions;

(ii) pH: 1.6;

(iii) Plating bath temperature: 60°C;

(iv) Current density: 50 A/dm^2; and

(iv) Solution flow rate: 1.0 m/sec.

Zn-Ni alloy plating was conducted in the examples of the invention that meet the limitation conditions of the invention described above and the comparative examples that do not meet the limitation conditions of the invention. Plating conditions other than those described above were the same for the examples and the comparative examples. Corrosion resistance test and plating adhesion test were then conducted for each sample. The corrosion resistance test was done by conducting a salt spray test of JIS Z 2371 for 240 hours. The plating adhesion test was done by a separation test in which cellophane tape was attached to the sample

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and the sample was bent by 180 degrees. The results are shown
in Table 1. Corrosion resistance and plating adhesion property
were evaluated as follows:

    ◎: excellent

    ○: good

    △: somewhat poor

    ×: poor

Table 1

	Sample No.	Ni molar concentration ratio	Bi^{3+} ion concentration (mg/1)	Plating layer Adhesion Amount (g/m^2)	Ni Content (%)	Corrosion resistance	Plating adhesion property
Example	1	0.4	92	30	11.6	◎	◎
	2	0.5	23	30	11.9	◎	◎
	3	0.5	45	30	13.0	◎	◎
	4	0.5	80	30	13.7	◎	◎
	5	0.58	5	30	10.5	◎	◎
Comparative Example	6	0.35	90	30	8.1	△	◎
	7	0.5	112	30	14.1	○	○
	8	0.67	0	30	11.8	◎	◎

    As can be seen from the comparative test results of Table
1, in sample Nos. 1 to 5 of the examples that meet the limitation
conditions of the invention, a Ni content of the plating layer
is within a proper range of 9 to 18%, and corrosion resistance
and plating adhesion property of the Zn-Ni alloy plating are
excellent. In sample Nos. 6, 7, 8 of the comparative examples,
on the other hand, either corrosion resistance or plating adhesion
property is inferior except sample No. 8. More specifically, in
sample No. 6 of the comparative example, a Ni molar concentration
ratio is 0.35, i.e., less than 0.4. Therefore, plating adhesion
property is excellent, but corrosion resistance is not so good.
Moreover, a Ni content of the plating layer is 8.1%, that is, less
than 9%. In sample No. 7, an excessive amount of Bi^{3+} ions over
100 mg/1 is added. Therefore, a Ni content is as high as 14.1%,

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but corrosion resistance and plating adhesion property are somewhat inferior. On the other hand, in the sample having a Ni molar concentration ratio of more than 0.6, a Ni content is as high as 11.8% even though Bi^{+3} ions are not added, and corrosion resistance and plating adhesion property are both excellent. However, this example belongs to the conventional technology and does not fall within the object of the invention.

(Effects of the Invention)

The invention provides the following effects by adding 1 to 100 mg/l of Bi^{3+} ions to a plating bath when a Zn-Ni alloy plated steel plate is manufactured by using a sulfate bath as a plating bath:

(i) By using a bath having a low Ni molar concentration ratio of 0.4 or more and less than 0.6, a γ single-phase Zn-Ni alloy plated steel plate containing 9 to 18 wt% of Ni in a plating layer was able to be obtained even at a current density of less than 100 A/dm^2 and a plating solution flow rate of less than 1.5 m/sec; and

(ii) By using a plating solution having a low Ni molar concentration ratio, an excellent Zn-Ni plating layer was able to be produced very economically without the need for special facility investment.

4. Brief Description of the Drawings

FIG. 1 is a graph obtained in an experimental process for obtaining the invention, showing the relation between a Bi^{3+} ion concentration (mg/l) in a plating bath and a Ni content (%) in a resulting plating layer at various Ni molar concentration ratios.

[FIG. 1]

Ordinate: Ni content in a plating layer (%)

Abscissa: Bi^{3+} ion concentration in a plating bath (mg/l)

Ni molar concentration ratio